

# (12) UK Patent Application (19) GB (11) 2 322 865 (13) A

(43) Date of A Publication 09.09.1998

(21) Application No 9704830.0

(22) Date of Filing 08.03.1997

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(51) INT CL<sup>6</sup>  
**E21B 43/25 , C09K 7/02**

(52) UK CL (Edition P )  
**C3U UDA U208 U210 U305 U319 U330 U604**  
**U1S S1248 S1269**

(56) Documents Cited  
**EP 0668339 A1      EP 0196632 A2      US 4939203 A**  
**US 4783492 A      US 3768566 A**

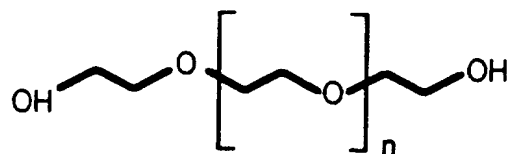
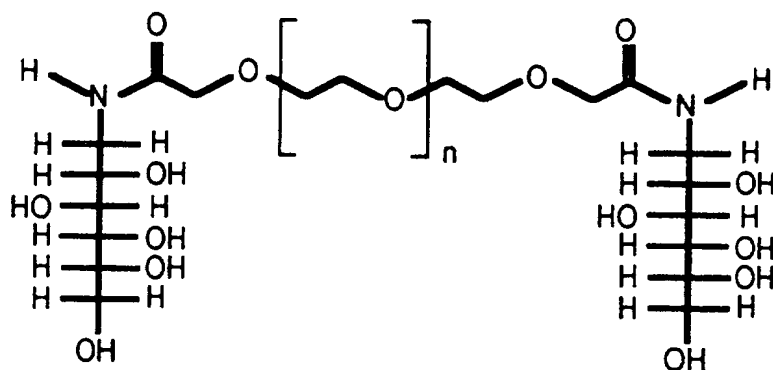
(58) Field of Search  
UK CL (Edition O ) **C3A A4 , C3U UDA**  
INT CL<sup>6</sup> **C09K 7/02 , E21B 33/138 43/02 43/25 43/26**  
**Online databases: WPI, CLAIMS**

(54) Abstract Title  
**Crosslinking agents for polymer solutions**

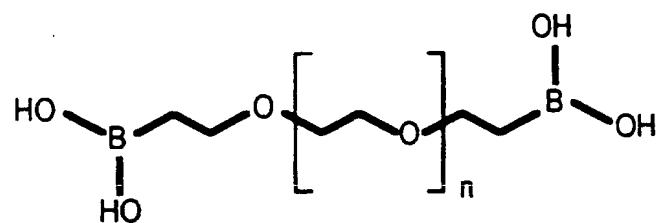
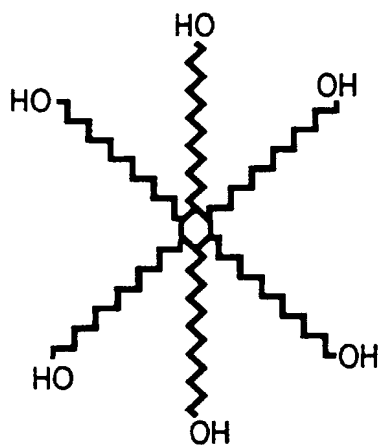
(57) Crosslinking agents for polymer solutions for fracturing, remedial and other operations within a wellbore are characterized by an extended linear spacer section between active groups which link to the polymer. The crosslinking agents can be advantageously applied to solutions with a polymer concentration below the overlap concentration. The crosslinking agents may be modified so as to have other advantageous properties, such as shale swelling inhibition, micelles formation and/or crosslinking delaying.

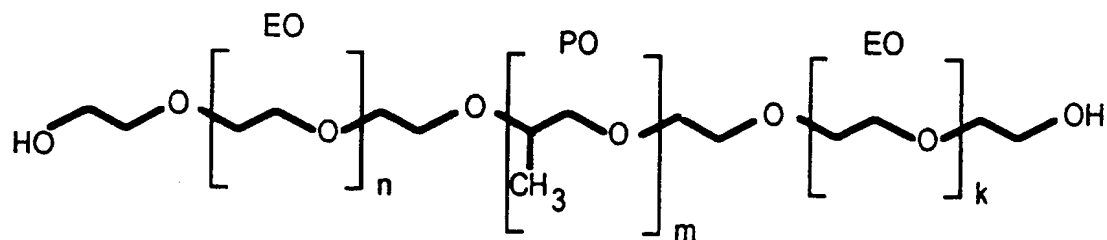
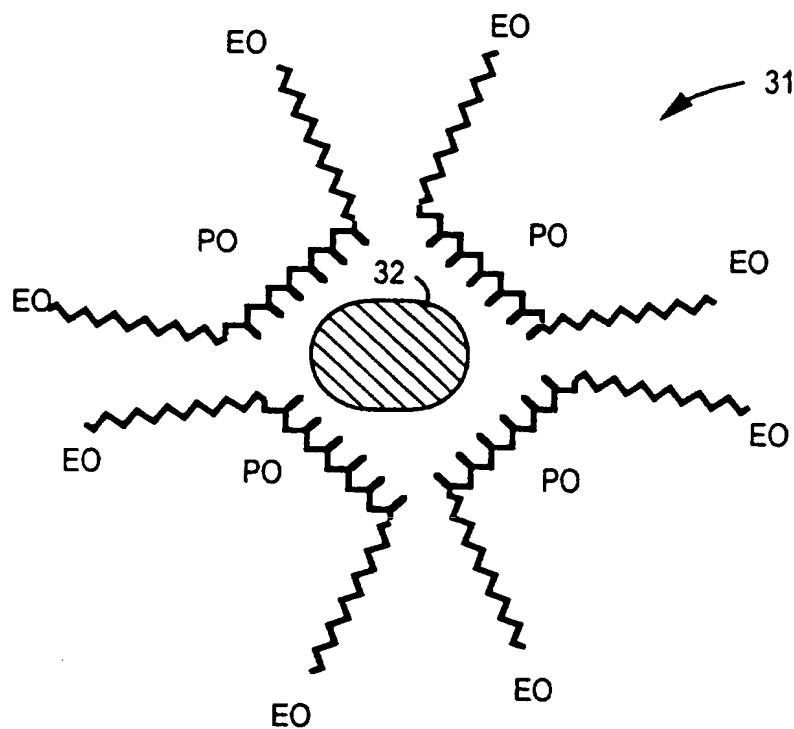
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*Fig. 1A**Fig. 1B*

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*Fig. 2**Fig. 4*

*Fig. 3A**Fig. 3B*

**Polymer gel for well operations**

The present invention relates to polymer compositions and methods  
5 for crosslinking polymers for use as a gelling system in well  
completion and oil recovery stimulation procedures.

**BACKGROUND OF THE INVENTION**

10 At various stages in the development, completion, and operation of  
natural hydrocarbon reservoirs, polymer based gelling systems are  
employed. In many of these procedures, which include fracturing  
subterreanean formations, modifying the permeability of  
subterreanean formations, or sand control, it is preferred to use  
15 crosslinked polymers.

The polymers employed are typically water soluble. Commonly used  
classes of water soluble polymers include polyvinyl polymers,  
polyacrylamides, cellulose ethers, or polysaccharides, in  
20 particular galactomannans (e.g., guar gum) and derivatives,  
thereof, or heteropolysaccharides (e.g., xanthan gum).

With respect to crosslinking agents, numerous examples of both,  
organic and inorganic compounds are known to those skilled in the  
25 art. Exemplary inorganic crosslinking agents include typically  
polyvalent metals, chelated polyvalent metals, and compounds  
capable of yielding polyvalent metals. Some of the more common  
inorganic crosslinking agents include chromium salts, aluminates,  
borates, gallates, titanium chelates, aluminum citrate, chromium  
30 citrate, chromium acetate, chromium propionate, and zirconium  
chelates or complexes.

Exemplary organic crosslinking agents include include aldehydes,  
dialdehydes, phenols, substituted phenols, and ethers. Phenol,  
35 resorcinol, catechol, phloroglucinol, gallic acid, pyrogallol,  
4,4'-diphenol, 1,3-dihydroxynaphthalene, 1,4-benzoquinone, hydro-  
quinone, quinhydrone, tannin, phenyl acetate, phenyl benzoate,  
1-naphthyl acetate, 2-naphthyl acetate, phenyl chloroacetate,

hydroxyphenylalkanols, formaldehyde, paraformaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, isobutyraldehyde, valeraldehyde, heptaldehyde, decanal, glyoxal, glutaraldehyde, terephthaldehyde, hexamethylenetetramine, trioxane, tetraoxane, 5 polyoxymethylene, and divinylether are some of the more typical organic crosslinking agents.

The known organic crosslinking agents are small molecules comprising less than 50 atoms. Usually these agents have a clearly 10 distinguishable central molecule or fragment with peripheral functional groups attached to it, giving the whole structure a more or less pronounced circular or spherical shape. Most of the known crosslinking agents require the polymer concentration to exceed a value  $c^*$  known as the overlap concentration. To reach  $c^*$ , 15 it is necessary to dissolve a large amount of polymer.

With regard to the aforementioned prior art it is seen as an object of the present invention to provide novel gellable compositions for well completion and hydrocarbon recovery 20 stimulation operations. It is a particular object of the invention to provide alternative crosslinking agents for such compositions. It is an even more specific object of the invention to provide a crosslinking agent for solutions having a polymer concentration below the overlap concentration  $c^*$ . 25

#### SUMMARY OF THE INVENTION

The above-mentioned objects are achieved by a composition as set 30 forth in the appended independent claims.

It is regarded as an important feature of the invention that the new polymer composition comprises a crosslinking agent with at least two terminal groups each able to bond with said polymer, 35 wherein said groups are connected by an essentially linear molecular chain.

Effectively the proposed crosslinking agents are composed of at least two active groups and an extended spacer section between them. The spacer section comprises preferably more than five carbon atoms and their substituents. More preferably, the length of the spacer section is more than 10, 20 or even 50 carbon atoms. An upper limit for the length of the spacer section is preferably defined by the onset of a coiling of the molecule. Depending on the chemical structure of the spacer section this upper limit can be any number between 20 and 1000, e.g. 20, 50 or 100.

10

It is seen as an advantage of the invention that the novel crosslinking agents can be successfully applied to a polymer solution with a concentration below the overlap concentration  $c^*$ .

15

The overlap concentration  $c^*$  is defined and effectively measured as the concentration at which polymer solution starts to gel, i.e., at which a rapid increase of the viscosity can be observed. The overlap concentration derives its name from modelling the polymers as spheres which (theoretically) begin to overlap at  $c^*$ .

20

It is seen as a further advantage that the novel crosslinking agents can be used under acid, neutral, and alkaline conditions (pH).

25

In a further embodiment of the invention, several spacer sections are attached to a central atom or molecular fragment so as to form an extended linear structure or a star shaped structure, if the number of spacer section exceeds two.

30

In yet another embodiment of the invention, the spacer section comprises hydrophobic and hydrophilic portions. Preferably, these portions are arranged so as to give the crosslinking agent the capability to form micelles. This embodiment has the advantage of acting as surfactant for otherwise insoluble particles, e.g.,

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particles created as the result of breaking. A breaking operation reduces the molecular weight of the (crosslinked) polymer and the viscosity of the gel. It is used for rapid clean-up of the well after fracturing. The polymer residues produced by the breaking

are often hydrophobic and tend to precipitate in an aqueous solution, hence, reducing the permeability of the fractures. Crosslinking agents according to this embodiment of the invention can solubilise those residues within the micelles.

5

In a further embodiment of the invention, the spacer comprises sub-units or groups which inhibit clay swelling, thus reducing the need to add large concentrations of salt (KCl).

- 10 When used as a fracturing fluid, the polymer gel preferably comprises a proppant to keep the fractures open after the hydraulic pressure is released. Known proppants include sand, resin coated sand, fused ceramics, sintered bauxite or zirconium oxides. Also a great variety of organic materials, such as nut shells, have been  
15 tried.

These and other features of the invention, preferred embodiments and variants thereof, possible applications and advantages will become appreciated and understood by those skilled in the art from  
20 the detailed description and drawings following hereinbelow.

#### DRAWINGS

- 25 FIG. 1A depicts the structural formula of a crosslinking agent in accordance with the invention.

FIG. 1B depicts the structural formula of a further crosslinking agent in accordance with the invention.

30

FIGs. 2-4 depict the structural formulae of further crosslinking agents in accordance with the invention.

35

#### EXAMPLES

The polymer used in the following examples is guar, which is employed in about 70 per cent of all fracturing operations in the



oil field industry. Guar consists of a mannose backbone with galactose side chains. The natural guar can be derivatized with propylene oxide to produce hydroxypropylguar (HPG). Further derivatives of guar include carboxymethylhydroxypropylguar (CMHPG). It is seen as lying within the scope of an average skilled chemist or chemical engineer to extend the examples given hereinbelow to other polymers, such as cellulose derivatives, like hydroxyethylcellulose (HEC) or hydroxypropylcellulose (HPC), or xanthan.

A guar solution at pH 10 containing 2.1 g/l guar in water, which is below the overlap concentration  $c^*$  of 2.4 g/l, and 0.288 g/l borate ( $B(OH)_4^-$ ) was prepared as a standard against which the performance of the novel crosslinking agents was tested. As crosslinking agents, polyethylene glycol (PEG) was used in a variant with a molecular weight of 1000 (PEG1000) and 600 (PEG600) amu, respectively. The PEG600 was further modified by adding gluconamide groups to both ends of the PEG molecule. The molecular structure of PEG and PEG digluconamide are depicted in Figs. 1A and 1B, respectively. Polyethylene glycol can form rigid, rod-like (linear) molecules as does PEG digluconamide and other derivatives of PEG mentioned hereinafter. This structure prevents intramolecular crosslinking, which is a major disadvantage of conventional crosslinking systems. The PEGs have a structure which can be made more or less hydrophilic by suitable arrangement of substituents along the chain; at the same time, difunctionality is readily introduced at the two ends of the chain. Furthermore, molecules such as the polyethylene glycols are known to be effective shale-swelling inhibitors.

The three test batches were tested to determine the gel strength. The gel strength was measured in accordance with the "bottle" test used in the industry as quasi standard. The results of the tests are summarized in table 1.

TABLE 1

2.1 g/l guar; 0.288 g/l borate; pH = 10; the gel strength increases from A to E

Batch No.	Crosslinker (Concentration)	gel strength	
		initial	after 24h
5			
1	-	C	-
2	PEG1000 (2.32 mmol/l)	D	D
3	PEG600-digluconamide (1.43 mmol/l)	E	E
10			

In another experiment the polymer concentration was successively reduced to a value below  $c^*$ . PEG digluconamide was used as crosslinking agent in a formulation equal to Batch No. 3 of table 1.

Guar Concentration (in g/l)	Gel strength
20	
4.8	H
3.6	G
2.4 ( $c^*$ )	E
2.1	E
1.8	C

25

The examples show that the novel crosslinking agents provide a significant increase in gel strength at a polymer concentration below the overlap concentration  $c^*$ . PEG digluconamides are a particular interesting example as having the potential of combining several useful features: PEG may act as powerful shale-swelling inhibitors, whereas the glucamine groups could provide a cross-link delay.

30

All gels break easily and cleanly with tetra-butyl ammonium persulfate at 60°C. Their thermal stability (as well as breaking properties) is more or less identical to that of conventional guar/borate gels. Simple vortex tests using a Waring blender were performed to determine an approximate viscosity of some of the

35

gels during formation. These tests suggested a delay in the formation of PEG-digluconamide containing gels, as reflected in the disappearance of the vortex some time after mixing in the blender.

5

Other examples of possible extended crosslinking agents (or spacers) as emerging from computational chemistry simulations include:

- 10 - PEG diboronic acids as shown in Fig. 2. This crosslinking agent can be synthesised readily from PEG1000, and obviates the need to use borate as a separate additive. The diboronate anion acts as the active crosslinker in this example. The molecules also aid in avoidance of intramolecular cross-linking of guar involving borate  
15 anions alone.

- PEG dialdehydes have aldehyde functionality at each end rather than borate. Also included in this group are PEG di-iodides/di-bromides and PEG isocyanates. They cross-link by a condensation  
20 reaction with cis-hydroxyl groups on guar. The diacetal so formed can be ruptured on acidification, thus breaking the crosslinks. It seems likely, however, that the cross-linkers formed from such dialdehyde molecules would probably not break under shear (being in this sense more like the zirconate and titanate crosslinkers),  
25 whereas the PEG + borate and PEG-diboronic acid crosslinkers could break (as is the case for the simpler borates). As with the polyether diols (PEGs), these molecules should also act as shale-swelling inhibitors, according to the results of molecular modelling simulations based on Monte Carlo methods.

30

- Pluronics as depicted in Fig. 3A are block copolymers comprising hydrophobic and hydrophilic portions. The peripheral hydrophilic portions are generally ethylene oxide (EO) units, while the central hydrophobic parts are typically comprised of  
35 propylene (or butylene) oxide (PO or BO) units. Hence these crosslinking agents have the capability to form micelles 31 at sufficiently high concentrations as illustrated by Fig. 3B. As in the case of the other molecules considered thus far, these

molecules can be expected to act as efficient clay-swelling inhibitors. An additional advantage of micelle-forming Pluronics as potential crosslinkers of guar polymers is that they may also prove effective at dissolving the insoluble mannose residues 32  
5 produced by oxidative breakers, provided their concentration is above the critical micelle concentration.

- Star PEGs are multi-armed PEGs made by polymerisation of ethylene oxide from a crosslinked divinyl benzene core, as  
10 schematically illustrated by Fig. 4. This large number of arms (typically ca. 120) permits the formation of hydrogels and leads to effective immobilisation on surfaces. A typical arm length is 130 - 170 EO units. Such molecules, either with added simple borate or with suitable end groups (as described above), have  
15 great potential to crosslink many guar molecules simultaneously.

## CLAIMS

1. Crosslinking agent for a gellable polymer solution for use in  
5 subterrean formations comprising molecules with at least two  
end groups each providing a linking site to said polymer or a  
secondary crosslinking agent, characterized in that said end  
groups are separated by an extended chain of atoms.
- 10 2. The crosslinking agent of claim 1, wherein the chain comprises  
at least 5, preferably at least 10, atoms.
3. The crosslinking agent of claim 1, wherein the chain is an  
essentially linear molecular fragment.
- 15 4. The crosslinking agent of claim 1, wherein the chain comprises  
repetitive units, said units preferably being ethylene oxide .
5. The crosslinking agent of claim 1, comprising hydrophilic and  
20 hydrophobic sections.
6. Gellable polymer solution for use within remedial operations in  
subterrean formations, comprising a crosslinking agent in  
accordance with claim 1.
- 25 7. The gellable polymer solution of claim 6, wherein the polymer  
solution has a concentration below the overlap concentration  
( $c^*$ ) .
- 30 8. The gellable polymer solution of claim 6, further comprising a  
proppant.
9. A method for treating subterreanen formation, comprising the  
steps of:  
35 - preparing a gellable polymer solution including a  
crosslinking agent in accordance with claim 1;

- pumping said solution into said subterreanen formation.

10. The method of claim 9, wherein the polymer solution has a concentration below the overlap concentration.

5

11. The method of claim 9, further comprising the step of adding a proppant to the solution.

10 12. The method of claim 9, further comprising the step of breaking the gel using a suitable chemical agent.



Application No: GB 9704830.0  
Claims searched: 1-12

Examiner: Alan Kerry  
Date of search: 30 May 1997

**Patents Act 1977**  
**Search Report under Section 17**

**Databases searched:**

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.O): C3U UDA; C3A A4

Int Cl (Ed.6): C09K 7/02; E21B 33/138, 43/02, 43/25, 43/26

Other: Online databases: WPI, CLAIMS

**Documents considered to be relevant:**

Category	Identity of document and relevant passage	Relevant to claims
X	EP 0668339 A1 (BAKER-HUGHES) see Claims 6-8; Examples 8-10	1 & 9 at least
X	EP 0196632 A2 (MINNETONKA) see Claim 1	1 at least
X	US 4783492 (DOVAN et al) see Claims 4 & 5	1 & 9 at least
A	US 4939203 (CITIES SERVICE OIL) see Claims 1, 9, 14, 15, 32, 44	
A	US 3768566 (ELY) see Claims 1, 5, 9, 10, 14	

X Document indicating lack of novelty or inventive step  
Y Document indicating lack of inventive step if combined with one or more other documents of same category.  
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A Document indicating technological background and/or state of the art.  
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